Electrospun fiber membranes from blends of poly(vinylidene fluoride) with fouling-resistant zwitterionic copolymers

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Abstract

Nonwoven super-hydrophobic fiber membranes have potential applications in oil–water separation and membrane distillation, but fouling negatively impacts both applications. Membranes were prepared from blends comprising poly(vinylidene fluoride) (PVDF) and random zwitterionic copolymers of poly(methyl methacrylate) (PMMA) with sulfobetaine methacrylate (SBMA) or with sulfobetaine-2-vinylpyridine (SB2VP). PVDF imparts mechanical strength to the membrane, while the copolymers enhance fouling resistance. Blend composition was varied by controlling the PVDF-to-copolymer ratio. Nonwoven fiber membranes were obtained by electrospinning solutions of PVDF and the copolymers in a mixed solvent of N,N-dimethylacetamide and acetone. The PVDF crystal phases and crystallinities of the blends were studied using wide-angle X-ray diffraction and differential scanning calorimetry (DSC). PVDF crystallized preferentially into its polar $\beta$-phase, though its degree of crystallinity was reduced with increased addition of the random copolymers. Thermogravimetry (TG) showed that the degradation temperatures varied systematically with blend composition. PVDF blends with either copolymer showed significant increase of fouling resistance. Membranes prepared from blends containing 10% P(MMA-ran-SB2VP) had the highest fouling resistance, with a fivefold decrease in protein adsorption on the surface, compared to homopolymer PVDF. They also exhibited higher pure water flux, and better oil removal in oil–water separation experiments. © 2018 Society of Chemical Industry

Supporting information may be found in the online version of this article.

Keywords: PVDF; SBMA; SB2VP; Zwitterion; Filtration; Electrospinning

INTRODUCTION

Alleviating safe drinking water scarcity is an important global challenge, especially in developing countries and in regions with a dry climate. Filtration of wastewater for re-use is favored here as it can be applied to common sources such as industrial wastewater outputs from petroleum extraction and refining,1–3 textile dyeing and finishing,4–6 food industries7–9 and even municipal wastewater10,11 to a more limited extent. Membrane fouling is defined as a decline in membrane performance due to the adsorption and accumulation of feed components, especially organic compounds, on the membrane surface. It is one of the main obstacles in increasing the feasibility and the efficiency of these membranes. Fouling can lead to substantial flux loss in a very short period of time. This problem could be tackled by introducing fouling-resistant properties into the membranes. Typically, hydrophobic membranes exhibit better mechanical and chemical stability, but suffer from more severe fouling due to the energetic driving force for water-soluble macromolecules such as proteins to adsorb on their surfaces. However, hydrophobicity is also important in some specific membrane water treatment applications such as oil–water separation and membrane distillation. While previous studies have found good candidates for this class of materials,12–15 through targeted design of functional, self-organizing polymers specifically for this application, better performance can be achieved. The most common approaches here are to either make use of constituents that will segregate to the membrane surface16–21 or to employ post-processing treatments.22–26

In this study, we examine hydrophobic membranes created from polymer blends which contain zwitterionics, and are fabricated into nonwoven fibrous mats by means of electrospinning. A zwitterionic polymer has both negative and positive charges bound to it allowing water molecules to be bound into a hydration layer around the zwitterionic groups, reducing the adsorption of foulants. Typically, zwitterionic groups are incorporated onto surfaces through surface grafting, where the membrane surface is first activated (e.g., by plasma treatment or irradiation) and then
exposed to a zwitterionic monomer. For instance, surface grafting of a zwitterionic monomer onto a poly(vinylidene fluoride) (PVDF) membrane in one study led to a 77% decline in protein adsorption along with a significant decrease in contact angle, indicating increased surface hydrophilicity. Another study, using a different grafting method and zwitterionic monomer but similar PVDF membranes, also showed an approximately 80% decrease in the adsorption of two proteins. This confirms that grafting of zwitterions onto PVDF creates a hydrophilic surface and improves fouling resistance, but the process requires several processing steps that add to manufacturing costs and alter membrane properties.

One approach to incorporating hydrophilic groups to membrane surfaces involves blending an amphiphilic copolymer additive with a hydrophobic commodity polymer during membrane manufacture by the well-established non-solvent-induced phase inversion (NIPS) process. The hydrophilic groups in the copolymer additive draw it to the polymer-water interface, whereas the hydrophobic repeat units anchor it onto the membrane. This method enables the formation of fouling-resistant membranes without any added manufacturing steps. Various groups have applied this approach using zwitterionic groups as the hydrophilic, fouling-resistant repeat units in the copolymer. Of these, only one focused on membranes prepared from PVDF, the membrane material of choice for many applications due to its chemical resistance and mechanical properties. However, the use of amphiphilic surface-segregating additives has been limited to membranes prepared by NIPS, which includes a water immersion step. This step may be crucial for the surface segregation of the copolymer. Thus, this blending approach has not been used much for membranes prepared by other methods.

Electrospinning is a popular fabrication method of filtration membranes among experimentalists but only a handful of studies have been done on electrospun fiber membranes with zwitterionic additives, mostly focused on biomedical and tissue engineering applications. Very little experimental work has been done with specific interest in filtration applications; this makes our study unique. In this study, we hypothesized that electrospun membranes prepared from blends of a hydrophobic base polymer, PVDF, with zwitterionic amphiphilic copolymers can lead to improved resistance to fouling. We also aimed to further understand how the use of these zwitterionic additives would change the crystallization of PVDF, and the physical, thermal and surface properties of resultant membranes.

As one component of our polymer blend used for electrospinning, we chose a commercial polymer, PVDF, that imparts the necessary mechanical strength to our membrane as well as hydrophobicity. For the zwitterionic blend partner, we synthesized two specialty copolymers that combine different types of repeat units along their backbones. The first unit is methyl methacrylate (MMA), common to both our copolymers, and was chosen to provide anchoring groups because it is known to be miscible with PVDF. Then we chose two different zwitterionic monomers, either sulfobetaine-2-vinylpyridine (SB2VP) or sulfobetaine methacrylate (SBMA), to copolymerize with MMA making a random copolymer. Our goal was to investigate the structure and fouling resistance properties of membranes comprising blends of specialty copolymers with PVDF, as a function of blend composition.

Using the technique of electrospinning, fibrous membranes were successfully fabricated from blends of PVDF and the copolymers. The morphology of fiber membranes of all blends was determined using SEM. The crystallographic information of the membranes was obtained using wide-angle X-ray scattering (WAXS) and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Thermal properties of the membranes were studied using TG and DSC. Protein adsorption propensity of the fiber mats was tested using epifluorescence. Blends of PVDF with both copolymers showed excellent fouling resistance.

**EXPERIMENTAL**

**Materials**

Pellets of PVDF (KYNAR® grade 740) were obtained from Arkema Chemicals Inc. (Colombes, France). Oil Red O was purchased from Sigma Aldrich (St Louis, Missouri). Poly(MMA-random-SBMA) and poly(MMA-ran-SB2VP) were synthesized using free radical polymerization following protocols found in previous studies. These two copolymers will be referred to by C-SBMA and C-SB2VP, which stand for “copolymer poly(MMA-ran-SBMA)” and “copolymer poly(MMA-ran-SB2VP),” respectively. Copolymer composition was characterized using 1H NMR spectroscopy using a Bruker Avance III 500 spectrometer (Bruker Optics Inc., Billerica, Massachusetts). C-SBMA contained 19 wt% SBMA, whereas C-SB2VP contained 18 wt% SB2VP.

Blends of PVDF with the copolymers were made by dissolving both components in a common solvent of N,N-dimethylacetamide (DMAC) and acetonitrile (7/3 v/v). Composition of these blends was varied by controlling the PVDF content. For PVDF blends with C-SB2VP, solutions were obtained with 100, 95, 90, 85, 80 and 0 wt% PVDF of the total polymer blend content. For PVDF blends with C-SBMA, only 100, 95, 90, 85 and 0 wt% PVDF formed well-dissolved solutions, due to relatively lower miscibility between PVDF and SBMA-containing copolymers. For all polymer blend solutions, first the PVDF pellets were dissolved in DMAC, using magnetic stirring for several hours at 90 °C. Once the PVDF dissolved, the temperature was lowered to 45 °C and the necessary amounts of acetonitrile and copolymer were added, with further stirring until clear solutions were obtained at 20% (w/v) polymer content in the spinning dope.

**Electrospinning**

Electrospinning was used to create nanofibers that yielded a non-woven fibrous mat about 8 cm in diameter. Electrospun fibers were deposited from polymer blend solutions at room temperature, at a flow rate of 2.0 mL h−1 controlled by a syringe pump (CADG5127-1EA, Sigma-Aldrich Inc., St Louis, Missouri), through a glass syringe of inner diameter 14.6 mm fitted with an 18-gauge (inner diameter 0.84 mm) stainless steel needle. A high-voltage power supply (ES30P-5w, Gamma High Voltage Research Inc., Ormond Beach, Florida) provided an accelerating voltage of 18 kV to the needle tip, while a flat, grounded collector plate rotating at 1 rpm was placed 20 cm away, with surface perpendicular to the needle. This resulted in an isotropic distribution of the fibers lying predominantly in the plane of the collector plate.

**Characterization**

Small pieces of the fibrous mats were mounted on standard SEM stubs and were coated with Au–Pd alloy for 90 s using a Cressington Sputter Coater 108 (Cressington Scientific Instruments, Watford, UK). The fiber morphology was examined using a Phenom G2 Pure SEM (Phenom-World BV, Eindhoven, The Netherlands) operating at 5 kV. The SEM images, Fig. 1a–h, were processed with the DiameterJ plugin of the application software ImageJ, to obtain...
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Figure 1. a–h) SEM images at magnification ×5000, for fibers spun at 20% (w/v) solution concentration. In (b–h), the nominal weight percent of the copolymer in the blend is given. Scale bars are 10 μm. (a) 100% PVDF; (b–d) PVDF and C-SBMA blends; (e–h) PVDF and C-SB2VP blends. (i) Histogram showing the distribution of diameters obtained from ImageJ for as-spun 95% PVDF/5% C-SBMA fiber mat, and the corresponding probability density function (black line). (j) Average diameter versus PVDF content in the blend, of all as-spun PVDF/copolymer fibers. PVDF, red diamond; PVDF/C-SBMA, blue triangles; PVDF/C-SB2VP, black circles.

Statistics about fiber size. DiameterJ converts the images into sharp black and white images and identifies pixel arrays corresponding to fibers, by using pattern recognition. Then the widths of these collections of pixels corresponding to fibers are counted and outputted as a histogram.

One-dimensional WAXS was performed on fibrous mats in reflection mode using a Philips PW 1830 powder diffractometer (Malvern PANalytical BV, Almelo, The Netherlands) operated at 40 kV and 45 mA, with X-rays of wavelength $\lambda = 0.1542$ nm (Cu K$_\alpha$). Fibrous samples were placed on single-crystal (100) Si substrates and were examined in $\theta/2\theta$ reflection mode (for $\theta$ the half-scattering angle) using a step scan interval of 0.02° per step and scanning rate of 0.01° s$^{-1}$ from $2\theta = 5$° to 40°. The scattered intensity from the empty Si holder was subtracted as background.

ATR-FTIR spectra for fibrous samples were acquired using a Jasco FTIR-6200 spectrometer (Jasco Instruments, Tokyo, Japan). The spectra were obtained using the instrument’s Spectra Manager software in absorption mode at 4 cm$^{-1}$ resolution with 256 scans co-added, between 400 and 4000 cm$^{-1}$. Background absorption of air was subtracted from the sample spectra to set the baseline.

A TA Instruments (New Castle, Delaware) Q500 series thermogravimetric analyzer was used to perform TG experiments from 25 to 800 °C at 20 °C min$^{-1}$ under 50 mL min$^{-1}$ N$_2$ gas flow. Sample sizes were 5–15 mg. Differential Scanning Calorimetric experiments were performed using a TA Instruments Q100 series DSC equipped with a refrigerated cooling system with N$_2$ protection gas flowing at 50 mL min$^{-1}$. The DSC cell was calibrated for heat capacity using a sapphire standard and for temperature and heat flow accuracy using an indium standard. Fiber samples were rolled up on a mandrel and placed in standard aluminium DSC sample pans using the “fixed-end” method described in our previous work$^{46}$ to ensure maximum contact and uniform heat flow. Sample
masses varied between 3 and 10 mg. DSC scans were performed following a heat–cool–heat cycle protocol on the samples in the range — 80 to 200 °C, at heating and cooling rates of 10 °C min⁻¹. The first heating ramp was used to erase thermal history and therefore only data from the second heating were used for analysis.

Membrane Performance
Protein fouling resistance of the fiber mats was investigated using a method adopted from the work of Seo et al. Fluorescein isothiocyanate-labeled bovine serum albumin (FITC-labeled BSA), a negatively charged foulant, was dissolved in phosphate-buffered saline (PBS), at a concentration of 5 mg L⁻¹, to create the test foulant solution. Then 5 cm × 5 cm pieces were cut from the fiber mats and soaked in the foulant solution for 10 min. Upon removal from the foulant solution, the mats were washed three times with fresh PBS and then visualized using an epifluorescence microscope (Olympus BX51 equipped with a DP70 microscope digital camera, Center Valley, Pennsylvania). Epifluorescence micrographs were acquired with a 20× objective lens using a standard green (U-N31001) filter set (Chroma Technology Corp., Rockingham, Vermont). Total fluorescence intensities of the images were calculated using ImageJ image analysis software.

To obtain the water permeance, water filtration was performed using an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm², connected to a 3.5 L dispensing tank. A pressure of 6 psi (0.041 MPa) was applied during the 30 min water filtration period, and the cell was kept stirred at 500 rpm using a stir plate. The weight of the permeate collected was automatically recorded every 30 s using a Scout Pro SP401 balance connected to TWedge 2.4 software (TEC-IT, Austria). Permeance through each mat was calculated by normalizing the average water flux by filtration pressure.

Oil–water separation tests were conducted using the same setup described above for water permeance measurements. Model oil-in-water emulsion comprised 5 g L⁻¹ soybean oil in deionized water, mixed with 0.02 g L⁻¹ Oil Red O dye for staining the suspended oil droplets in red. The mixture was subject to 3 min of rigorous blending for obtaining a homogeneously stained, stable oil-in-water emulsion. To quantify the oil rejection of the fiber mats, the oil-in-water emulsion was filtered through the mats at 6 psi (0.041 MPa) pressure. The first milliliter of permeate was disposed of, and the following 5–6 mL of permeate was collected to obtain the rejection, defined as

\[ R = \frac{100 (C_f - C_p)}{C_f} \]  

Here, \( R \) is the Oil Red O dye rejection (%), \( C_f \) is the feed concentration (g L⁻¹) and \( C_p \) is the permeate concentration (g L⁻¹). Dye concentration in the feed and permeate was quantified by measuring the UV absorbance at 355 nm using a Thermo Scientific Genesys 10S UV–visible spectrophotometer equipped with a high-intensity xenon lamp and dual-beam optical geometry. Oil rejection was assumed identical to dye rejection since the Oil Red O dye stains the oil droplets.

RESULTS AND DISCUSSION
Fig. 1 shows typical SEM images of electrospun fibers obtained from the polymer blends. Uniform smooth fibers, free of defects such as beads or cracks, were obtained at all compositions (Figs 1(a)–(h)). The average diameters of the fibrous samples were calculated using ImageJ software, and show a skewed Gaussian distribution. An example distribution (average diameter histogram for 95% PVDF and 5% C-SBMA) is shown in Fig. 1(i). It was observed that the average size of fibers shifted towards smaller diameters as the copolymer fraction increased (Fig. 1(j)), and the average fiber diameters of all blends span a narrow range of 300 to 450 nm.

WAXS results are shown in Figs 2(a) and (b) for as-spun mats supported on single-crystal (100) silicon wafers. Intensity is normalized to the maximum in each scan. Background subtraction was performed using the empty Si wafer, which sometimes led to incomplete removal of the silicon peak around 33°. The pure copolymers, containing 0 wt% PVDF, show two amorphous halos, the first appearing around 14.5° (0.61 nm) and the second appearing near 29° (0.31 nm). Absence of any sharp reflections indicates the amorphous nature of the pure copolymer components. In fibrous blends of PVDF with either of the copolymers, crystal diffraction peaks characteristic of the γ-phase and β-phase of PVDF were observed (Figs 2(a) and (b)). These results are consistent with other reports of PVDF crystal phase in electrospun fibers, which confirm the tendency for PVDF to form polar phases rather than nonpolar α-phase.

Generally, for both copolymers, as the copolymer content in the blend increases, PVDF crystallization is hindered. The crystallinity from WAXS analysis, \( \Phi_{c, WAXS} \), was calculated from

\[ \Phi_{c, WAXS} = \frac{A_{cryst}}{A_{total}} \]  

where \( A_{cryst} \) is the area of crystalline peaks after amorphous halo subtraction and \( A_{total} \) is the total area under the WAXS curve, within the 2θ range explored. In Fig. 2(c) the WAXS crystallinity (filled symbols) is compared to the crystallinity of the blends developed by melt crystallization (open symbols). The melt crystallinities were calculated from DSC endotherms taken at 10 °C min⁻¹, from the second heating after controlled cooling at the same rate. The heat of fusion of 100% PVDF was taken as 104.6 J g⁻¹. The degree of crystallinity was found generally to increase as the PVDF fraction in the blend increases though that trend is muted in the melt crystallized materials. Melt crystallization of the blends results in greater crystallinity than seen in as-spun fibers. Figure S1 of the supporting information shows via infrared spectroscopy that the α crystallographic phase is favored when crystallizing PVDF from the melt.

Figures 3(a) and (b) show ATR-FTIR spectra for as-spun PVDF/C-SB2VP and PVDF/C-SBMA, respectively. The spectra of pure copolymers, C-SB2VP and C-SBMA, are shown as the topmost spectra, and display almost identical features. Two characteristic peaks appear for both copolymers at around 1146 and 1724 cm⁻¹, corresponding to S=O asymmetric stretch and O=C=O ester carbonyl stretch, respectively. In agreement with the literature, a few as-spun fibers that contain PVDF display strong characteristic crystal peaks of β-phase (1275 cm⁻¹), with weak α-phase peaks (614 and 763 cm⁻¹) and γ-phase (811 and 1234 cm⁻¹). Upon melt crystallization of these fibers, peaks corresponding to α-phase become much more pronounced and peaks associated with β- and γ-phases diminish (supporting information, Figs S1(a) and (b)). Similar to neat PVDF, PVDF blended with zwitterionic copolymers crystallizes preferentially into β-phase crystal conformation in as-spun fibers, or into non-polar α-phase when melt crystallized.
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Figure 2. Normalized WAXS intensity versus scattering angle, $2\theta$, at the PVDF/copolymer compositions given: (a) PVDF/C-SB2VP blends; (b) PVDF/C-SBMA blends. Crystalline $\gamma$- and $\beta$-phase PVDF reflections are marked with their Miller indices.° (c) Degree of crystallinity as a function of PVDF content in the blend, for as-spun fibers (filled symbols) from WAXS analysis and melt crystallized materials (open symbols) from DSC analysis. Red diamonds, PVDF; blue triangles, PVDF/C-SBMA; black circles, PVDF/C-SB2VP. Symbols at the origin refer to the copolymers C-SBMA and C-SB2VP which are non-crystalline.

Figure 3. Normalized (at 876 cm$^{-1}$ for blends that contain PVDF, 48 at 1146 cm$^{-1}$ for pure copolymers) FTIR spectra for as-spun fibers, from bottom to top by PVDF/copolymer ratio. (a) PVDF and its blends with C-SB2VP showed a difference of absorption at 1723 cm$^{-1}$: as the fraction of PVDF increased, this peak shifted slightly (ca 3–4 cm$^{-1}$) to higher wavenumber and decreased in amplitude. (b) PVDF blends with C-SBMA showed almost no absorption at 1723 cm$^{-1}$, compared to the pure copolymer. For C-SB2VP (Fig. 3(a)), the peak at 1724 cm$^{-1}$ can be seen clearly in the spectra of the blends with a slight shift to a higher wavenumber, 1727 cm$^{-1}$, compared to the pure copolymer. The peak at 1146 cm$^{-1}$ in the blends appears as a shoulder, and also undergoes a slight shift (1148 cm$^{-1}$) compared to the pure copolymer. These small shifts are within the wavenumber resolution of the spectra. The peak amplitude of both features is seen to decrease with decreasing copolymer fraction. The same features are present in the spectra for C-SBMA blends as well, but due to the low absorption of C-SBMA, these amplitudes are extremely small, making them almost imperceptible at the presented scaling.

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As shown in Fig. 4, TGA indicates that, after any solvent loss, PVDF starts degrading at around 350 °C while the pure copolymers start their degradation process at much lower temperature, around 200 °C. The degradation of PVDF occurs as a single-step transition, whereas both copolymers show two degradation steps before 425 °C, corresponding to their two constituents. In almost all blends, the degradation step heights of each component scale with the absolute amount of that component initially present in the material mixture (supporting information, Fig. S2). For homopolymer PVDF and some of the blends, it is observed that the mass does not drop all the way to zero as temperature increases above 450 °C.
Figure 4. TGA curves of mass remaining versus temperature during heating at 20 °C min⁻¹. The PVDF/copolymer blend ratio is given. (a) PVDF blends with C-SB2VP; (b) PVDF blends with C-SBMA. A stepwise decrease of mass remaining with increase of copolymer can be seen at temperatures above 300 °C for the blends. Degradation temperature decreases as copolymer content increases in both blends. (c) The amount of solvent retained in as-spun fibers (determined from the mass loss between room temperature and 200 °C). Red diamond, PVDF; blue triangles, PVDF/C-SBMA; black circles, PVDF/C-SB2VP.

Figure 5. Heat flow rate versus temperature at heating and cooling rates of 10 °C min⁻¹. Top stack of curves, cooling; bottom stack of curves, heating. Exotherms presented with upward deflection. (a) PVDF blends with C-SB2VP; (b) PVDF blends with C-SBMA. PVDF/copolymer ratio is indicated above (cooling) or below (heating) the curves. Curves have been displaced vertically for clarity. Because PVDF char tends to stick to the TGA basket upon melting. This prevents the N₂ purge gas flow from removing the burnt-up material through the exhaust. But in the blends of PVDF/C-SB2VP (Fig. 4(a)), the mass does eventually drop to zero for all compositions, indicating that addition of SB2VP completely eliminates the sticky nature of the material even when it is present at low percentage. In contrast, for SBMA, the amount of sticky residue in the pan decreases gradually with increasing SBMA fraction and completely vanishes at 15 wt% or more of SBMA (supporting information, Fig. S3). Figure 4(c) shows that as-spun pure copolymers retained 2.5–3.5 wt% of bound solvent in the as-spun fibers. PVDF homopolymer retained very little bound solvent, about 0.4 wt%. The amount of solvent retained in the blends varied between these limits, being always larger than the retained solvent in homopolymer PVDF and always less than the solvent retained in the pure copolymers.

Results from DSC (Fig. 5) show that the crystallization exotherm areas upon cooling (and the related melting endotherm areas) decrease with an increase of the copolymer content. In homopolymer PVDF, crystallization from the melt occurs at ca 135 °C and...
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Figure 6. Representative epifluorescence microscope images of the mats acquired after FITC-labeled BSA adsorption. Copolymer composition in the blends is indicated in (b–g). Green color indicates fluorescent foulant protein caught on the membrane. (a) 100% PVDF; (b–d) PVDF blends with C-SB2VP; (e–g) PVDF blends with C-SBMA. Best fouling resistance was achieved for PVDF blended with 10% C-SB2VP. The scale bars are 200 μm.

Figure 7. Mean fluorescence intensity of the blends, calculated from epifluorescence microscopy images. Error bars refer to the standard deviation of at least five randomly selected areas chosen for each mat. From left to right: PVDF homopolymer, gray bar; three blends of PVDF with C-SB2VP, bars in shades of green; three blends of PVDF with C-SBMA, bars in shades of red. The composition of copolymer in the blends is indicated below the bars. Intensity shows a fivefold decrease of foulants retained for PVDF blended with 10% C-SB2VP along with satisfactory results for all the samples tested.

Melting peaks for these crystals are observed in heating at ca. 165°C. In the C-SB2VP blends (Fig. 5(a)) both the crystallization peak position and the peak onset temperature shift towards lower temperatures when the fraction of this copolymer increases. In the C-SBMA blends (Fig. 5(b)) the trend in crystallization peak temperature and peak onset is less clear.

To investigate the resistance of the electrospun mats to protein adsorption, we immersed them in FITC-labeled BSA foulant solution, and then imaged the mat surface using epifluorescence microscopy. Figures 6 and 7 show the acquired images and the mean fluorescence intensity, respectively. Adsorbed protein appears green in the images due to the fluorescent labeling. Mats made from copolymer blends exhibit lower green coloring compared to the 100% PVDF sample, demonstrating a reduction in protein adsorption on the mats for both copolymers. Error bars represent the standard deviation from at least five randomly selected areas chosen for each mat. Addition of C-SB2VP copolymer to PVDF at 5 wt% in electrospun fiber mats led to promising adsorption resistance, whereas at 10 wt% C-SB2VP addition the adsorption resistance rose to excellence (Fig. 6). This indicates that presence of zwitterionic groups on the mat surface imparts substantial fouling resistance against proteins. On the other hand, at 15 wt% concentration in the polymer blend, miscibility between C-SB2VP and PVDF was partial. This likely resulted in phase separation and an inhomogeneous, patchy distribution of C-SB2VP on the mat surface, leading to poorer fouling resistance. Use of C-SBMA in the blends also prevented protein fouling to a good
substantially improved compared to that of the 100% PVDF mat. The blend containing 10 wt% C-SB2VP also exhibited higher pure water flux, and better oil removal in oil–water separation experiments. This information enables us to build a knowledge base that directs the design and enhancement of additional polymers and electrospinning processes for targeted applications including self-cleaning materials, breathable fabrics, membrane distillation and oil–water separation.

### Table 1. Pure water permeance and oil rejection of 10% C-SB2VP blend and control 100% PVDF membranes

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>Pure water permeability (L m⁻² h⁻¹ bar⁻¹)</th>
<th>Oil rejection (%)</th>
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<tr>
<td>10% C-SB2VP</td>
<td>653 ± 187</td>
<td>87 ± 8</td>
</tr>
<tr>
<td>100% PVDF</td>
<td>476 ± 38</td>
<td>67 ± 12</td>
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**Figure 8.** Permeate samples obtained after filtering Oil Red O dye-stained oil-in-water emulsion through the mats showing feed, permeate after filtration by 100% PVDF and permeate after filtration by a blend of PVDF with 10% C-SB2VP.

### CONCLUSIONS

We have successfully shown that the zwitterionic copolymers blended with PVDF are suitable for production of electrospun nonwoven fiber membranes. We have carried out an investigation of the thermal behavior of the blends, including the study of crystal formation and melting. The crystallinity of the blends showed a decrease with increasing copolymer fraction. The addition of copolymers reduced the onset temperature of degradation of the blends compared to homopolymer PVDF. It was also seen that the blends tend to retain slightly more solvent than PVDF. Both zwitterionic copolymer blends showed substantial decrease in amount of protein foulant retained. We successfully showed that addition of 10% C-SB2VP to PVDF is ideal for application as a filtration membrane, since it introduced a fivefold decrease in amount of adsorbed foulants, compared to homopolymer PVDF fiber mats which served as a control. The blend containing 10% C-SB2VP also exhibits higher pure water flux, and better oil removal in oil–water separation experiments. This information enables us to build a knowledge base that directs the design and enhancement of additional polymers and electrospinning processes for targeted applications including self-cleaning materials, breathable fabrics, membrane distillation and oil–water separation.

### ACKNOWLEDGEMENTS

Support for this research was provided by the Tufts Collaborates seed grant program of Tufts University, and by the National Science Foundation, Polymers Program of the Division of Materials Research, under DMR-1608125, and through the MURI Program under DMR-0520655 which provided thermal analysis instrumentation. This work was conducted at Tufts University by interns DC, AD, CM and KS who are equal coauthors of this work. The authors thank Prof. Hyunmin Yi of the Department of Chemical and Biological Engineering at Tufts University for access to the epifluorescence microscopy facility and guidance in experimental design, and Eric Liu for instrumental training. The authors also thank Mr. Jonathan Minoff of Tufts University, and our American Sign Language interpreters, Mark Riley, Francine Arnold and Megan MacDonald.

### SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

### REFERENCES
